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The Role of Interphase Phenomena in the Processes of Ion Transport Through Liquid Membranes

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The principal interphase phenomena accompanying the transfer of a substance through liquid membranes (chemical reactions, the formation of supersaturation and microheterogeneity zones, spontaneous interphase convection), which are related to many important characteristics of the kinetics of ion transport, have been examined. By influencing these processes it is possible to control the rate of trans-boundary transfer.
The bibliography contains 61 references.

CONTENTS

I. Introduction 559
II. Chemical reactions 559
III. Supersaturation and microheterogeneity zones and condensed interphase films 561
IV. Spontaneous interphase convection 562

I. INTRODUCTION

Liquid membranes are finding increasing application for the extraction, concentration, and separation of substances of different kinds,[1,2] and also for modelling individual functions of biological cell membranes.[3-5]

A liquid membrane is a layer of an organic phase separating two aqueous solutions. This layer may be thick or extremely thin, and may be free or deposited on a solid porous material which gives the resulting system mechanical stability. A large number of emulsions of the water–oil–water type are also used. Processes using these emulsions are called membrane or emulsion extraction.[2]

Irrespective of how the membrane process is organised, a common feature is the presence of "accepting" and "delivering" phase interfaces; extraction takes place at the first of these, and re-extraction at the second. Another common feature is that the physicochemical phenomena at the boundaries of the immiscible liquids and in the extremely thin layers adjoining them, and also at the boundaries with the solid, play an extremely important and sometimes a decisive role in ion transport.

These interphase phenomena include chemical reactions, adsorption, surface association, the formation of supersaturation and microheterogeneity zones (SMZ), the formation of condensed interphase films (CIF), and spontaneous interphase convection (SIC). In thin membranes or when organic phases fixed to solid carriers are used, the formation of inverse micelles and aqueous channels becomes important. These phenomena are closely related to one another and to the processes of ion transport. A good example is provided by spontaneous interphase convection, a phenomenon whose study may give results of considerable scientific and practical importance, in particular the development of the cheapest methods of intensifying ion transport in heterogeneous systems.

The aim of the present review was to examine the principal interphase processes accompanying the transfer of substances through liquid membranes and their inter-relationships and interdependence.

II. CHEMICAL REACTIONS

The liquid phase of a membrane usually contains a carrier, that is an active component which interacts with ions to give lyophilic compounds soluble in the organic phase. The carriers may be neutralic, acidic, or basic substances, which react with the ions being extracted by ion exchange, the formation of coordination compounds, or both mechanisms simultaneously (chelate formation). In a number of cases, for example when salts of amines and quaternary ammonium bases are used as carriers, an important role is played by the formation of ion pairs (contact pairs and pairs separated by water molecules) and hydrogen bond formation. The transfer of metal ions by macrocyclic crown ethers and cryptands takes place as a result of the inclusion of the metal cation in the cavity of the macro-ring, in which it is retained, usually, by ion–dipole interaction forces. Donor–acceptor interactions and the formation of coordinate bonds may also play an important role in this case (for example in the transfer of actinide and lanthanide ions).

Thus as in the "classical" method of extraction,[6,7] in membrane methods using carriers, mass transfer is accompanied by chemical reactions, whose rate may have a significant influence on the intensity of the entire process of mass exchange. As in extraction, it is possible to distinguish processes involving the previous formation of the compound being extracted (that is a compound of the component being extracted and the carrier), the actual formation of the extractable compound, chemical transformations of the latter during its transport through the membrane, decomposition of the extractable compound at the other side of the membrane, and subsequent reactions involving its decomposition products.

Experience accumulated in the study of the kinetics of chemical reactions in extraction[7] indicates that the formation and rupture of hydrogen bonds, proton transfer, and ionic and molecular association or dissocation do not limit the rate of trans-membrane transfer, but may influence it concentration dependence by changing the individual resistances to the diffusion of each of the components in the membrane phase and in the aqueous solutions surrounding it.

The formation (and decomposition) of coordination compounds of the carriers and the components being extracted are slower, and therefore create an additional (chemical) resistance, taken into account by appropriate equations for the additivity of the phase resistances.[7] In this case, within homologous series of organic carrier reagents, as in extraction,[7] correlations may be observed between the stabilities of the compounds and the rates of trans-membrane transfer. The formation (and decomposition) of intra-complex kinetically inert compounds is even slower.[7] These reactions, which often determine the rates of extraction and re-extraction, may also limit the rate of trans-membrane transfer,[2,8] It must be borne in mind, however, that the role of the diffusion resistance of the organic phase is greater in a membrane process than in extraction, particularly in those cases where this phase is fixed on a solid support, which prevents the development of natural or forced convection.

Thus in many cases of practical importance it is necessary to take account of the rates of chemical reactions and the resistance to transfer which they create. The method used to take account of ion transport processes (the form of the equation for the additivity of the phase resistances) and, which is more important, the method used to identify these processes, depend to a significant extent on the mechanism and topology of the chemical reactions.

Chemical reactions are most frequently localised not in the entire volume or a multiphase system but only in an extremely small part of it, called the reaction zone. Exceptions are encountered only in very slow homogeneous chemical reactions, which generally are not of interest for processes of practical importance. The reaction zone coincides with the region where the main diffusion resistances are concentrated, that is with the interphase region, so that all the phenomena which alter the hydrodynamic conditions or the composition of the liquids in the interphase region should also influence the kinetics of the chemical reactions and the intensity of the mass-exchange process as a whole.[7]

One of the most obvious methods of intensifying ion transport is by increasing the rates of the chemical reactions using added catalysts. In the discussion of the mechanism of their action, two different types of interphase reactions are considered: surface and bulk (next to the surface).[7] In the transport of ions through membranes, reactions of the first type create the so-called "small merry-go-round", and those of the second type create the "large merry-go-round".[3,9] The role of the "small merry-go-round" in ion transport through a phase interface is still disputed, although the question has been widely discussed in the study of the kinetics of extraction[7] and membrane processes,[3-5,9] and has also been examined by specialists in the synthesis of organic substances in two-phase systems.[10]

The most definite conclusions reached in the study of the mechanism of formation of extractable compounds reduce to the following:[7] a surface reaction, that is a reaction involving adsorbed substances, is always accompanied by a corresponding reaction next to the surface, the contribution of the first of these being greatest at low concentrations of reagents having surface-active properties. In non-steady-state processes, the surface reaction predominates at low exposures of the phases, but subsequently the second reaction channel (the "large merry-go-round") develops, and its contribution increases.

A method has been developed for calculating the contributions of the two reaction channels,[11] and the conditions controlling each of them have been found. In particular, it has been shown for the reactions between copper ions and hydroxyoximes that extremely small quantities of added ionic surface-active substances (SAS) have a greater influence on the rates of surface reactions than on the rates of reactions localised in layers of the aqueous phase next to the surface. Anionic SAS increase the rate of both the formation and the decomposition of the copper hydroxyoximate, whereas cationic SAS decrease the rates of these reactions (see Table and Refs. 12 to 14). The acceleration factor reached 8, and the retardation factor 25, so that by using SAS it is possible to change the rate of the process by a factor of 200.[11,12]

The influence of SAS on the parameters of the extraction and re-extraction of copper in systems containing 2-hydroxy-5-octylbenzophenone oxime.[11]

SAS	c_{SAS}, M	Extraction*			Re-extraction**		
		F	P_s	P_v	F	P_s	P_v
Sodium lauryl sulphate	10^{-5}	1.1	0.38	0.62	2.1	0.40	0.60
	$5\cdot10^{-5}$	1.5	0.45	0.55	3.6	0.43	0.57
	10^{-4}	2.5	0.63	0.37	4.5	0.58	0.42
	$5\cdot10^{-4}$	4.3	0.88	0.12	7.2	0.69	0.31
	10^{-3}	4.8	0.91	0.09	8.2	0.74	0.26
Cetyltrimethyl-ammonium bromide	10^{-5}	0.8	0.38	0.62	0.4	0.32	0.68
	$2\cdot10^{-5}$	0.63	0.21	0.79	0.3	0.32	0.68
	$5\cdot10^{-5}$	0.52	0.15	0.85	0.2	0.25	0.75
	$5\cdot10^{-4}$	0.13	0.10	0.90	0.05	0.20	0.80
	10^{-3}	0.11	0.07	0.93	0.04	0.11	0.89
2-(α,α-Dimethyl-benzyl)-4-methyl-6-nitrosophenol	10^{-4}	2.3	0.30	0.70	3.0	0.33	0.67
	$2\cdot10^{-4}$	4.8	0.25	0.75	3.5	0.21	0.79
	$8\cdot10^{-4}$	6.0	0.15	0.85	7.8	0.15	0.85
	$2\cdot10^{-3}$	10.0	0.09	0.91	12.0	0.17	0.83
	$5\cdot10^{-3}$	12.0	0.07	0.93	15.0	0.12	0.88

Notation: F is the acceleration factor; P_s and P_v the contributions of the surface and volume reactions respectively; and c_{SAS} the SAS concentration.

* Conditions: pH 3.0, copper concentration in the aqueous phase 0.11 M.

** Conditions: pH 2.4, copper concentration in the organic phase 0.031 M.

Two explanations of the influence of these modifying agents are of interest. The first is based on the assumption that the stages determining the rates of the chemical reactions involved in the formation or decomposition of the extractable complexes take place within the electrical double layer, in which the nature of the distribution of the potential is influenced by ionic SAS. If these stages involve intermediate positively charged complexes, it follows that anionic SAS, as a consequence of electrostatic interaction, will increase the surface concentration of these complexes, leading to an increase in the reaction rates. The opposite picture for the adsorption of cationic SAS.

The second explanation, which reduces to so-called micellar catalysis, assumes the existence of supersaturation and micro-heterogeneity zones under non-equilibrium conditions in the interphase region. Adsorption on microheterogeneous particles, and a specific distribution of the substances between the bulk and micellar phases, may lead to an appreciable change in the overall reaction rate.[15,16]

It is important to note that "catalytic" effects of identical sign (but not absolute magnitude) have been observed not only in the transport of ions through "free" interfaces but also when an organic medium fixed on a porous hydrophobic material (polyethylene, Teflon) is used.[17]

Finally, it is necessary to discuss the mechanism of action of modifying agents which do not have strong surface-active properties but which themselves are capable of extracting ions weakly but rapidly. These substances include, for example, 2-(α,α-dimethylbenzyl)-4-methyl-6-nitrosophenol (ONP). The Table shows that increase in the ONP concentration leads to an increase in the contribution of the reaction next to the surface, which becomes the predominant reaction at high ONP concentrations. The acceleration is most probably due to the appearance of an additional reaction channel in the layers next to the surface in the organic phase; when ONP is present, an exchange reaction between the *o*-nitrosophenol residue (R′) and the hydroxyoxime residue (R) begins:

$$CuR_2' + H_2R \rightleftarrows CuR_2 + H_2R'$$

The production of additional reaction channels in the aqueous and organic phases is the main reason for the increase in the rate of the transfer of cations by alkyl hydrogen phosphates[18] and tri-n-octylphosphine oxide.[19]

In organic syntheses in two-phase systems, this mechanism of the acceleration of ion transport is known as "transport catalysis".[10]

III. SUPERSATURATION AND MICROHETEROGENEITY ZONES AND CONDENSED INTERPHASE FILMS

The transport of ions through a phase interface is accompanied by the transfer of the solvent, in particular water, since dehydration is not instantaneous. It penetrates to a definite depth, depending on the ratio between the diffusion coefficients and the rate constants of dehydration.

The existence in the interphase region of hydrodynamic fluctuations which are due to the statistical nature of the turbulent pulsations produced under the influence of the mixing assemblies or as a result of the existence of Marangoni–Gibbs effects, leads to corresponding fluctuations in the depth of penetration of the reaction and the concentration fields. The local values of these concentrations may exceed the solubility limit, leading to supersaturation and the formation of microheterogeneous regions of the "water in oil" and "oil in water" type. This is associated with the phenomenon, frequently observed in extraction, of the production of a "fog", extending from the phase interface into the volume of the phases. The formation of SMZ provided a basis for the development of the concept of the "sandwich" structure of the interphase region in the transport of ions through a liquid–liquid phase interface.[7,17]

According to these ideas, the interphase region includes the adsorption layer and the adjoining supersaturated and microheterogeneous layers layers of the organic and aqueous phases, whose properties and extent depend significantly on the direction and intensity of the ion transport. The assumption that there is a dynamic interphase structure, in contrast to the static structure usually considered, has made it possible to explain successfully the electrical properties of the interfaces in various liquid–liquid systems, and also a whole series of unusual kinetic relationships (saturation of the mass fluxes through the "delivering" phase interface,[7,17,20] the extremal dependence of the rate of ion transport on the concentration of the complexes being transferred in the organic phase,[17] the loss of the sensitivity of the mass fluxes to change in the intensity of mixing,[17,20,21] etc.).

The production of SMZ next to the boundaries of liquid–liquid systems has a marked influence on the intensity of mass exchange. On the one hand, it decreases the trans-boundary mass flux as a result of the shielding of the surface and the decrease in the concentration gradients at right angles to the boundary, and on the other hand it increases the rate of extraction as a result of the production of tangential gradients in the interphase tension and the development of spontaneous interphase convection under the influence of Marangoni–Gibbs effects. It is true that this mechanism appears distinctly only at free boundaries, so long as the microheterogeneity zones do not undergo phase transformations. The latter are sometimes observed at strictly definite (critical) concentrations of the substance being extracted in the aqueous solutions[7,17,20] and are accompanied by an abrupt change in the rate of ion transport as a result of sharp changes in the rheological properties of the interphase boundaries. Thus SMZ have a definite aggregation (or kinetic) stability. When they lose this stability, they are converted into viscous CIF under some conditions, and into solid CIF under other conditions.[7,22]

An important consequence of the formation of SMZ in ion transport through liquid membranes is a change in the equilibrium conditions at the interphase boundaries and hence in the overall diffusion resistance calculated from the equation for the additivity of the phase resistances. For steady-state transport processes, these local boundary conditions remain unchanged with time, but they do not coincide with the conditions found on the basis of known distribution coefficients. For non-steady-state processes, the equilibrium boundary conditions change with time, since the composition and width of the SMZ do not remain constant, but depend on the magnitude of the trans-boundary fluxes.

If the thickness of the membrane is smaller than the width of the SMZ (the latter may reach $10^{-4}-10^{-3}$ cm),[17,22] the liquid is microheterogeneous throughout the entire thickness of the membrane. The quantity of the substance being transferred in it may then differ considerably from that calculated from data on the equilibrium for macroscopic phase volumes.

The production of SMZ is apparently the initial stage in the formation of aqueous "channels" in impregnated membranes, and is the reason for electrical breakdown in electrodialysis through extraction membranes.[23] If these conclusions are correct, one method of combatting breakdown may be by introducing into the system substances which increase the rate of dehydration of the ions.

The formation of CIF influences the rate of ion transport to an even greater extent than the formation of SMZ. This phenomenon is characteristic of ions which tend to undergo hydrolysis and hydrolytic association, so that their extraction is accompanied by the formation of "medusae" ("beards", "caps"), which bring about a marked deterioration in the separation of the emulsions into layers and decrease the efficiency of mass-exchange equipment.[7,17] The formation of CIF (gels) is the main reason for the decrease in the efficiency of ultra- and micro-filtration equipment and the non-rationality of the use of large pressure drops.[24,25] The mechanism of the production of gels in ultra- and micro-filters is of course different from that in extraction. The result is the same in both cases, however, namely a sharp increase in the diffusion resistance, and sometimes a decrease in the selectivity, so that it is necessary to find methods of combatting concentration polarisation of this type.

The regular features of the formation of CIF at the boundaries of liquid–liquid systems have been studied in detail for the ions of metals in the central part of the periodic system of the elements (Zr, Hf, Nb, Ta, Ti, Si, etc.).[22] There is no doubt that the conclusions reached can be extended to processes involving liquid membranes. The methods used to prevent the formation of CIF are more varied in this case than in filtration. A decisive role is played by the state of the ions in the aqueous solution and by the nature of the carrier,

the modifying reagents, and the organic solvents, whose selection can reduce film formation to a minimum.[22] It is also possible to control the processes of CIF formation by adding surface-active substances to the aqueous solutions, and also by applying a potential difference between the phases.[22]

IV. SPONTANEOUS INTERPHASE CONVECTION

Because of its considerable scientific and practical importance, the phenomenon of spontaneous interphase convection has recently been attracting increased interest.[26,27,32,33] The phenomenon is of fundamental importance, since it provides a source of information on the regular features of the production and development of the self-organising dissipative structures in non-equilibrium open systems[28,29] and on the mechanisms of the processes of the change from "order" to "chaos".[30] The practical importance of this phenomenon is due to the promising possibilities provided by the development of highly effective low-energy methods for intensifying mass-exchange processes. Published experimental data indicate that the breakdown of hydrodynamic stability, leading to the appearance of conductive movements in the interphase region, can increase the rate of ion transport by several orders of magnitude as a result of the breakdown of the diffusion boundary layer and the decrease in concentration polarisation.

Spontaneous interphase convection may be due both to local changes in the bulk properties of the phases in the region next to the surface and to the loss of mechanical stability by the interphase boundary as a result of local breakdown of the balance of the tangential forces acting on it. A decisive influence on the local changes in the bulk and surface properties is exerted by chemical reactions, processes of adsorption and surface association, the formation of zones of extended non-uniformity, such as SMZ and CIF, and the action of an electromagnetic field.[7,27]

Allowance for the role of each of these factors, not to mention their combinations, often encounters fundamental difficulties, since at present there are no adequate models for many processes of this type. For an adequate treatment of the phenomenon of SIC it is possible to use the methods of the thermodynamics of irreversible processes. A thermodynamic analysis makes it possible to obtain in the most general form expressions for the criteria of hydrodynamic instability and to reveal the importance of various perturbing parameters.[28,31] At the same time, the use of these criteria for a quantitative interpretation encounters serious difficulties, since it requires the experimental determination of phenomenological coefficients, and this is an incorrect aim at the existing level of knowledge of SIC.

From the viewpoint of the quantitative interpretation of the regular features of SIC and the study of its mechanisms, it is apparently preferable to use the classical hydrodynamic approach, based on the solution of the differential equations of the momentum balance together with the equations of state relating the pressure, density, and temperature, and the equations of convective heat transfer and diffusion. The role of the various interphase processes responsible for the breakdown of hydrodynamic stability is taken into account by introducing perturbations not only into the main equations but also, when necessary into the corresponding boundary conditions. The analysis of the stability involves the determination of the conditions which lead to an unlimited increase in the perturbations in relation to the coordinates and time.[31,32]

To develop methods for controlling the hydrodynamic instability, it is necessary to know the properties (bulk or surface) whose local changes lead to its appearance. An analysis of published data shows, however, that it is not always possible to distinguish clearly the contribution of these factors. At the same time there is no doubt that local breakdown of the balance of the tangential forces acting on the interphase surface has a decisive influence on the production of the SEC for processes of ion transport through liquid membranes with free boundaries. For these processes, the study of the role of capillary and surface electrical forces is of the greatest interest from the practical viewpoint.[34–38]

Capillary instability (Marangoni–Gibbs instability) is due to local fluctuations in the magnitude of the interphase tension. The physical significance of the mechanism of the production of instability in this case has been clearly demonstrated in Refs.31, 33–38, where it was shown that for a non-equilibrium distribution of the interphase tension in at least one of the phases there should be a movement leading to the appearance at the interphase surface of a friction force tending to balance the interphase tension gradient. The changes with time in the interphase tension gradients unavoidably lead to perturbations with time in the velocity field, which may either be quenched or increased with the passage of time. The last case corresponds to hydrodynamic instability.

The production of stable or unstable hydrodynamic conditions depends on the existence of a critical value of the interphase tension gradient, and when this is exceeded, the perturbations of the velocity field produced by the fluctuations in the interphase tension begin to increase with time. The critical value of the interphase tension gradient can be characterised by the so-called Marangoni critical number (Ma_{cr}). It has been shown that if $Ma < Ma_{cr}$ the perturbations of the velocity field are quenched with time, and when $Ma \geqslant Ma_{cr}$ the movement becomes unstable.[33,36]

An attempt has been made[39] to establish a quantitative correlation between the rate of interphase transfer and the Marangoni number under conditions of non-equilibrium distribution of the interphase tension. Subsequently, a rigorous theoretical foundation for the correlation obtained[40] was derived from an analysis of the kinetics of mass transfer in a thin film with a specified interphase tension drop at the mobile interphase boundary. The acceleration factor has been determined[41–43] for interphase transfer in a two-phase system formed by two plane-parallel layers of the immiscible liquids, where the fluxes of each of them had an ordered circulation structure. The circulation structures were described by solving the Navier–Stokes equations for a given tangential force at the interphase boundary. This analysis gave the dependence of the acceleration factor η on the Peclet number Pe. For small Peclet numbers, the relationship $\eta \sim Pe^2$ is fulfilled, whereas as $Pe \to \infty$, $\eta \sim Pe^{0.5}$. Since the rate of convective movement and hence the magnitude of Pe are proportional to the interphase tension gradient, the interphase transfer can be intensified by altering the interphase tension.

The existence of a tangential component of the intensity of the electric field acting on the interphase boundary leads to the product of so-called electrocapillary instability, whose regular features cannot be described without taking account of the ionic nature of the reagents being transferred through the phase interphase or adsorbed on it. A large amount of experimental data indicating the existence of an instability of this kind has been published. An example is given in Ref.44, where is was shown that the oscillator movements of an oil–water phase interface are produced only if the organic phase contains a dissolved electrolyte. This system can serve as a simple and clear example of the existence of positive and negative feedback controlling the hydrodynamic instability. The existence of this feedback is a necessary condition for the production of SIC.[28] The positive feedback is provided by the adsorption of SAS

(cetyltrimethylammonium chloride) and the negative feedback by the interphase transfer of ions.

The basic principles of the instability of this system were described in Ref.37, which examined a simple model in which the appearance of SIC was due to the action of electrostatic forces. The main result obtained in the work cited is that for ionic mass transfer between two immiscible electrolyte solutions, the hydrodynamic stability of the interphase boundary is controlled not only by the Ma number but also by an electrical factor.[37] This factor may either stabilise or destabilise the phase interface.

The search for correlations between the electrochemical and hydrodynamic parameters under conditions of hydrodynamic instability was dealt with in Ref.45. A one-to-one correspondence was established between the appearance of ordered flow, induced by ion transfer, and oscillations in the electrical voltage. In this connection, mention may be made of an extremely interesting method for visualising dissipative structures[46] in the chemisorption of carbon dioxide by aqueous solutions of amines. By using a polarisation-optical method it has been possible to record the formation of convective cells in the form of spindles with cylindrical symmetry.

The Marangoni instability produced by the adsorption of substances forming condensed interphase films at a phase interface has been studied.[47-54] The conditions were found for the production of SIC in the form of both ordered and random flow, and their characteristic parameters were determined. The experiments were carried out in a system formed by mercury and an electrolyte solution containing an added SAS, which formed a condensed interphase film.[47] In this system, third-order polarographic maxima are observed, due to the tangential movement of the interphase boundary as a result of the formation of regions with an increased interphase tension. Breakdown of the hydrodynamic stability took place only on the adsorption of substances with a high attraction constant.

A study of adsorption at a toluene–water boundary during the extraction of tetrachloropalladate anions by trioctylamine[48] made it possible to record the formation of a non-uniform CIF with the simultaneous appearance of spontaneous surface convection, produced by local changes in the interphase tension as a result of the non-uniform supply of the substance to individual regions of the interphase surface.

An extremely marked increase in the rate of mass exchange under conditions of hydrodynamic instability was recorded[49-54] in a study of SIC during the extraction of metals in systems of practical importance. An increase in the rate of ion transport by more than two orders of magnitude was observed. A large amount of experimental materials showed that the breakdown of the hydrodynamic stability of the interphase boundary and the appearance of spontaneous movements in the liquid in the interphase region always take place when the extraction process is accompanied by the formation of CIF.

A typical example is provided by the extraction of the lanthanides and various actinides from nitric acid solutions by solutions of di-2-ethylhexyl hydrogen phosphate in non-polar diluents such as octane, decane, and toluene.[7] A study of the kinetics of mass transfer in a system consisting of two layers of phases in contact in tubes with a diameter of 1–3 mm without deliberate mixing showed that extremely intensive SIC takes place for several tens of seconds after the phases are brought into contact. The coefficients of mass transfer reach values of $(5-8) \times 12^{-2}$ cm s^{-1}. The breakdown of hydrodynamic stability was due to the non-uniform formation of CIF at the interphase surface. The interphase tension gradients produced lead to an oscillator movement of the interphase boundary and to intensive movement of the liquids in the interphase region, which is gradually quenched and stops completely when the film produced forms a continuous layer covering the entire interphase surface and reaches a certain strength level. If part of the interphase film is subsequently removed, mass transfer through the renewed sections of the surface again leads to destabilisation of the interphase boundary and the appearance of intensive movements in the phases.

Spontaneous rupture of the continuous interphase film and the production of movement of the interphase boundary and the adjoining layers of liquid are frequently observed. Sometimes this process is periodic in character.[53] The production of hydrodynamic instability is influenced significantly by the concentrations of the reacting components. Critical values have been detected for the metal and extracting agent concentrations, above which mass transfer unavoidably leads to breakdown of the hydrodynamic stability of the interphase boundary and the appearance of spontaneous surface convection. The concentration ranges of the existence of SIC are fairly wide, from 10^{-1} g litre^{-1} to several tens and even hundreds of g litre^{-1} with respect to the metal concentration and from 10^{-3} M to 1–1.5 M with respect to the concentration of the extracting agent.

In these extraction systems it was experimentally established for the first time that the rate of ion transport under SIC conditions depends on the ratio of the thicknesses of the layers of the phases in contact. There exists a critical value of the ratio of the thicknesses, at which extremely high rates of mass transfer are observed.[52-54] Thus breakdown of the ratio of the thicknesses of the phases acts as another destabilising factor. This conclusion is consistent with the results of theoretical studies[35] which show that the ratio of the thicknesses of the layers of the phases in contact influences the dimensions of the range of stable states. Cine- and photo-recording in cells with a width of 1 cm has revealed the structure of the hydrodynamic fluxes in the interphase region.[53] At all ratios of the thicknesses of the layers of the phases in contact different from the critical ratio, SIC appears in the form of circlation cells. The calculated values of the Reynolds number for currents of this kind did not exceed 150. At a ratio of the layer thicknesses equal to the critical ratio, the nature of the movement of the liquid changes sharply. Intensive eruptions, penetrating to a depth of 2–3 cm into the aqueous phase, are produced. The maximum rate of movement of the liquid reaches several tens of cm s^{-1}, and the value of the Reynolds number lies in the range 200–2000. Forced mixing of the phases did not have a negative influence of the parameters of mass transfer under SIC conditions, and merely decreased slightly the time interval before it began in those cases where these conditions were not established immediately after the phases were brought into contact. Other conditions being equal, the surface of even relatively large drops with a diameter of 3–5 mm was found to have a higher hydrodynamic stability than a planar phase interface. For this reason, ion transport through a planar interphase surface was more intensive. The addition of small quantities of various SAS, for example dodecanol, initiated the production of SIC.

The above material represents the main ideas regarding the role of SIC in the transfer of substances through free interphase boundaries. The question of the role of SIC in the constrained movement of liquids and contrained diffusion in systems with non-free interphase boundaries remains open. For its solution, it is necessary to take account of the existence of long-range surface forces[55] in the analysis of the role of hydrodynamic instability in the processes of transport through impregnated liquid membranes and multiple emulsion membranes.

Published experimental data indicate that hydrodynamic instability can also lead to an appreciable intensification of ion transport in systems with non-free interphase boundaries.[56-60] Thus the passage of an alternating electric current through impregnated membranes increases the rate of ion transfer,[58,59] probably due to the appearance of convective movements in the membrane phase. The dependence of the rate of ion transport on the frequency of the alternating current is described by a curve with a maximum.[59] The authors of Ref.60 consider it more promising to use an alternating current with a frequency of 1 Hz, and they assume that a current with this frequency acts directly on the liquid–liquid interphase surface, leading to the production of tangential movement on it.

An attempt to establish the relationship between the characteristic dimensions of the pores in an impregnated membrane and the rate of transfer[61] showed that increase in the pore diameter leads to a significant increase in the effective values of the diffusion coefficients in the membrane, apparently as a result of the production of convective movements in the pores.

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Thus many characteristic features of the kinetics of ion transport through liquid membranes are related to interphase processes of different kinds. The existing views on these processes do not yet give a completely consistent picture. At the same time there is no doubt that systematic studies in this field can give results of scientific and practical importance which should lead to a deeper understanding of the regular features of ion transport and to the solution of the problems of intensifying and controlling the rates of membrane processes.

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